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SUBJECT Application of Lithium-Aluminum Hydride in Microsynthesis of Organic Compounds Containing Radioactive Carbon

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1. Izvestiya Acsdemii Nauk SSSR, Otdeleniye Khimicheskii Nauk, July-August 1953, No 4, Page 587.

a. "In order to investigate radioactive isotopes it is necessary in most cases to prepare a pure chemical substance which contains in its molecules radioactive atoms. Many such scientific research projects have been done; however, in each case pure chemical substances containing several milligrams of a highly radioactive substance were available. The prospect of dealing with a microquantity of radioactive substance was of great interest to scientists working in that field.

b. "In microsynthesis of compounds possessing radioactive atoms, a lithium-aluminum hydride can be of great value because of its great substitute qualities. Lithium-aluminum hydride of late is more frequently applied in chemical synthesis since it is a most suitable substitute compound. A molecule of lithium-aluminum hydride contains comparatively large amounts of hydrogen. Because of this fact it secures very effective substitute qualities in addition to comparatively minor losses of the said reagent.

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c. "... major reaction based on substitution where lithium-aluminum hydride is used can be carried out with a very good yield -- at room temperature. There are no by-products in this reaction. From reactions based on substitution of lithium-aluminum hydride with aldehydes, ketones, composed ethers, carbonic acids, acid anhydrates, and lactones (containing in their molecules radioactive elements) corresponding alcohols can be obtained.

d. "When lithium hydride containing a radioactive atom is prepared and subjected to the synthesis as a lithium-aluminum hydride it may be used effectively as a substitute in order to obtain tritium. It is possible, of course, to combine both variants simultaneously. Lithium-aluminum hydride was used in our work as a substitute in order to obtain the substances containing a radio active carbon, C^{14}."

e. Experiments

(1) Synthesis of lithium-aluminum hydride

(a)"This synthesis is carried out in diethyl ether of diethylglycol. Diethyl ether of diethylglycol is prepared according to reaction:

$CLCH_2CH_2OCH_2CH_2CL + 2C_2H_5OH \rightarrow C_2H_5OCH_2CH_2OCH_2CH_2OC_2H_5 + 2HCL$.
$(HCL + KOH \rightarrow H_2O + KCL)$.

450 grams of kalium hydroxide is dissolved in 900 milliliters of ethyl alcohol (190^{0} proof). To this solution 350 grams of $\beta \beta$ dichlorine diethyl ether is added (a two liter flask is used).

(2)" $\beta \beta$ dichlorine diethyl ether may be obtained as follows:

(a)" $2CH_2 = CH_2 + CL_2O \rightarrow CLCH_2CH_2OCH_2CH_2CL$

The mixture of ethyl alcohol, kalium hydroxide and $\beta \beta$ dichlorine diethyl ether is heated under reflex for a 24 hour period. It is admitted that at the very beginning reaction is vigorous with the alcohol boiling intensely. For this reason a large beaker containing cold water should be used to cool the flask. After the reaction is completed a solid substance is separated from the liquid with a Buchner funnel and glass filter. Part of the liquid was distilled at a boiling point of 185^{0} centigrade to 189^{0} centigrade. The diethyl ether of diethyleneglycol was dried with metallic sodium for 24 hours and was then redistilled. As a result of this synthesis 125 grams of diethyl ether of diethyleneglycol was obtained (31 percent yield as compared with the theoretical yield). Boiling point of the ether was 187^{0} C; d 15/15 0.9150; n 20/0 1.414.

(b)"Lithium hydride which has to be used for the synthesis should contain at least 80 percent of a radioactive product. (The lithium hydride which we used in our work was produced in our local plant.) Prior to using lithium hydride for the reaction it was decomposed by water:

$LiH + H_2O \rightarrow LiOH + H_2$

(c)"A weighted quantity of lithium hydride was placed in a flask equipped with a separation funnel and a mercury manometer (pressure meter). Results of the reaction were determined by the pressure of hydrogen and its quantity. According to the reaction one milligram of lithium hydride releases 2.8 milliliters of hydrogen under normal conditions.

(d)"The table below (NI) shows the results of the analysis of radioactive substance in lithium hydride.

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[redacted]

Experiments	Quantity of Lithium Hydride	Volume of Hydrogen Under Normal Conditions	Content of Radio Active Substance
1	72.0 milligrams	188 milliliters	93%
2	74.8 milligrams	194 milliliters	93%
3	62.4 milligrams	157 milliliters	90%
4	51.0 milligrams	139 milliliters	95%

As the above analysis shows, the average content of radioactive substance of plant manufacture was 93 percent. This was completely satisfactory for our work. Aluminum chloride used was freshly sublimed [sic].

(e)"Before beginning the synthesis we prepared a so-called 'infection'. This was done as follows: We put 0.5 grams of pulverized lithium hydride in a test tube. To this we added two milliliters of diethyl ether of diethyleneglycol. To these ingredients, which we stirred slowly and constantly, we added 0.5 grams of aluminum chloride in 3 milliliters of the same ether. Lithium-aluminum hydride was produced according to the reaction:

$4\ LiH + AlCl_3 \xrightarrow{Ether} LiA8H_4 + 3LiCl_3$

8.9 grams of lithium hydride pulverized (#200) were poured into flask number 2. The infected ether [mentioned above] in flask number 1 was poured into flask number 2. Into this we poured very slowly 2.9 grams of aluminum chloride dissolved in 50 milliliters of diethyl ether of diethyleneglycol. In order to obtain the best results of reaction it is advisable to wait for five or six hours. The solution of lithium-aluminum hydride in ether can be separated from lithium hydride which didn't take part in the reaction -- the same applied to aluminum chloride (by means of separator funnels). The concentration of lithium-aluminum hydride in ether was determined by water treatment. The purity of lithium aluminum hydride was determined by the same means. In both cases several milligrams of lithium-aluminum hydride were placed into a flask of known volume and the temperature increased. This indicated the concentration of the solution. The reaction with water was as follows:

$LiALH_4 + 4H_2O \longrightarrow Li(OH) + AL(OH)_3 + 4H_2$

According to this reaction 2.4 milliliters of hydrogen under normal conditions corresponds to 1 milligram of lithium-aluminum hydride.

(3) Synthesis of Radioactive Methyl Alcohol

(a)"This synthesis was based on lithium-aluminum hydride's affinity to the substitution of carbon dioxide for the methyl alcohol. As a raw material for synthesis of radioactive methyl alcohol [redacted] used radioactive barium carbonate ($BaC^{14}O_3$). The initial research concerned with methods of synthesis was performed with regular raw materials [not radioactive]. Synthesis of methyl alcohol from carbon dioxide was done with vacuum glass equipment.

(b)"The 50 milliliter solution of 0.3% lithium-aluminum hydride in diethyl ether of diethyleneglycol was poured into a reaction flask. To the generator, carbon dioxide, 0.5 grams of barium carbonate ($BaC^{14}O_3$) was added 0.5 milliliters of Cu, then a funnel was filled with chemically pure sulfuric acid. Air was first pumped from the generator of carbon dioxide, then from the reaction flask. By pouring drops of sulfuric acid from the funnel to the generator

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radioactive carbon dioxide was released. The reaction was as follows:

$$BAC^{14}O_3 + H_2SO_4 \longrightarrow BASO_4 + H_2O + C^{14}O_2$$

(c)"Radio active carbon dioxide after passing the calcium chloride tube filled up the entire set. When the set was filled with radioactive carbon dioxide a stirrer was used. Decrease in pressure was noted immediately which showed the beginning of the reaction:

$$4C^{*}O_2 + 3\ LiALH_4 \longrightarrow LiAL(OC^{*}H_3)_4 + 2LiALO_2$$

The above reaction was carried out at a room temperature of 20^C centigrade. The total volume of the reaction set used was 500 milliliters. The pressure dropped to 90 millimeters of mercury.

(d)"According to Mendelayeev's equation it was easy to determine how many molecules of carbon took part in the reaction. This equation is as follows: PV NRT

$$N = \frac{PV}{RT} = \frac{90 \cdot 500}{6.2 \cdot 104.23} = 0.0025 \text{ molecules}$$

(e)"As a result of the [illegible]ction radioactive carbon dioxide was completely substitute[illegible]. A negligible quantity of remaining radioactive gas was drained into a trap.

(f)"The separation of radioactive methyl alcohol was completed according to the principle of substitution by the radioactiv[illegible] methoxyl group of lithium-aluminum hydride of an inactive methoxyl complex of methyl alcohol:

$$LiAL(OC^{*}H_3) + 4\ CH_3OH \longrightarrow LiAL(OCH_3)_4 + 4C^{*}{}_3OH$$

In order to accomplish this, 50 milliliters of methyl alcohol were poured into the reaction flask with a separator funnel. This mixture was stirred for six hours by using an induction device. When methyl alcohol was introduced to the mixture (in addition to the exchange reaction) another reaction took place between methyl alcohol and the lithium-aluminum hydride which didn't take part in the original reaction. This reaction was as follows:

$$LiALH_4 + 4CH_3OH \longrightarrow LiAL(OCH_3)_4 + 4H_2$$

Because of this reaction it was necessary, to stop the addition of methyl alcohol, to cool down the reacting mixture with liquid nitrogen, and to pump out generated hydrogen.

(g)"The contents of the reactor flask were then transferred to the distilled flask and radioactive methyl alcohol was separated from diethyl ether of diethyleneglycol. The big difference in the boiling points of these two compounds permitted complete separation and very satisfactory results. The test of radioactive methyl alcohol was determined with $BaC^{14}O_3$. The radioactivity of $BaC^{14}O_3$ was checked."

2. Analysis and comment

a. In the second and third chapters G I Felisov submits details relative to synthesis of methyl iodide and ethyl alcohol, both compounds possessing radioactive carbon tracer. As raw materials for synthesis of radioactive methyl alcohol Felisov used red phosphorous and crystallic iodine according to the equation:

$$3C^{14}H_3OH + PI_3 \longrightarrow 3C^{14}H_3I + P(OH)_3$$

b. Raw materials used for synthesis of radioactive ethyl alcohol were: radioactive methyl iodide and paraformaldehyde. The following reactions

*carbon tracer

show how Felisow synthesized radioactive ethyl alcohol. (Radioactive C^{14} belongs to the methoxy group CH_3).

$$C^{14}H_3I + Mg \rightarrow C^{14}H_3MgI;\ C^{14}H_3MgI + HCHO \rightarrow C^{14}H_3CH_2OMgI;$$

$$C^{14}H_3CH_2OMgI + H_2O \rightarrow C^{14}H_3CH_2OH + MgI(OH)$$

c. Final synthesis of the ethyl alcohol with radioactive carbon in hydroxy group was accomplished by substitution of radioactive ethyl-acetic ether and lithium hydride. The first step consisted in the preparation of radioactive barium acetate:

$$BaC^{14}O_3 \xrightarrow{H_2SO_4} C^{14}O_2CH_3MgI \xrightarrow{C^{14}O_2} CH_3C^{14}OOMgI \xrightarrow[Ba(OH)_2]{H_2O}$$

$$(CH_3C^{14}OO)_2BA\ (CH_3C^{14}OO)_2BA + C_2H_5OH \xrightarrow{H_2SO_4} CH_3C^{14}OOC_2H_5 2CH_3C^*OOC_2H_5 +$$

$$LiALH_4 \rightarrow LiALH_4 + LiAL(CH_3C^*H_2O)_4 LiAL(CH_3C^*H_2O)_4 + CH_3CH_2OH \rightarrow$$

$$LiAL(CH_3CH_2O)_4 + CH_3C^*H_2OH$$

d. The significance of this work is that Felisow synthesized originally:

(1) Lithium-aluminum hydride in diethyl ether of diethyleneglycol.

(2) Microsynthesis and separation of radioactive methyl alcohol containing C^{14} (carbon tracer).

(3) Ethyl alcohol radioactive with carbon tracer in methoxy group.

(4) Microsynthesis of aceto-ethyl ether with carbon tracer from barium acetate.

(5) Microsynthesis of radioactive ethyl alcohol containing carbon tracer in hydroxyl group.

(6) Synthesis of two isotopes of isomer acetaldehyde.

e. The paper is written in clear and simple form. Each step is a logical one in the field of chemistry. The author claims to have obtained radioactive substances as described above, but the interesting feature is his claim to have a control of carbon tracer in a group and in such quantities as desired.

f. It appears that this research was conducted on a purely academic basis with no preconceived conclusion in mind.

g. From the methodology pursued in the above research, [redacted] top Soviet chemists have a good knowledge of radioactive materials.

h. They claim that the work completed was original research. [redacted] the Soviets have top flight men who are comparable to US scientists, but feel that their second team is not composed of the well rounded personnel as is found in the US. [illegible] Felisow lauds is not [redacted] difficult. Any representative US chemist with adequate equipment could carry out the [illegible] little difficulty.

i. [redacted] Felisow and other Soviet chemists engaged in this experiment, have utilized foreign scientific papers. The article does, however, suggest original work and results.

- end -

*carbon tracer

[redacted]